



Thermodynamic modeling of the Pb + Bi melt evaporation under various pressures and temperatures

Nikolay Barbin^{a,*}, Dmitry Terentiev^a, Sergey Alexeev^{a,b}, Tatyana Barbina^b

^a Ural Institute of the State Fire Fighting Service of EMERCOM of Russia, 22 Mira Str., 620062 Ekaterinburg, Russia

^b Ural Federal University, 19 Mira Str., 620002 Ekaterinburg, Russia

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ABSTRACT

The composition of the vapor phase and the partial pressures of vapor components have been defined at pressures from 10^2 to 10^7 Pa and in the temperature range from 500 to 3000 K. Diagrams of liquid–vapor phase equilibria for the Pb–Bi system have been constructed. A good agreement between experimental results and the carried out calculations on the Pb–Bi phase diagrams is observed.

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1. Introduction

Molten metals and their vapors have found an increasing application as working bodies and heat-transfer media in various high-temperature power installations [1]. Processes occurring at evaporation of metals are of interest for vacuum metallurgy applications (alloying, purification of metals) [2] and nuclear power engineering (purification of heat-transfer liquid metals by distillation) [3].

The lead–bismuth alloy is a perspective heat-transfer medium for nuclear power units [4]. Data on the vapor pressure and liquid–vapor phase boundaries for lead–bismuth melts at pressures from 1 to 10^5 Pa are given in the article [5], however, the composition of the vapor and the partial pressures of its components are not defined.

Such experimental researches of metallurgical systems are complicated by the reaction conditions (high temperatures, difficulties of determination of the concentration of components, etc.). The method of thermodynamic modeling is often used for the investigation of the metal melt equilibrium vaporization.

2. Computational method

The thermodynamic modeling (TM) consists in the thermodynamic analysis of the equilibrium state of systems in whole (a

complete thermodynamic analysis). Here thermodynamic systems are conditionally selected material areas which interaction with environment is reduced to the exchange of heat and work. The application of TM allows to simulate quantitatively and predict compositions and properties of complex heterogeneous, multielement, multiphase systems in the wide range of temperatures and pressures, taking into account chemical and phase transformations [6–8].

Calculation methods have been developed on the basis of variational principles of thermodynamics:

- (1) Of all the permissible values of moles of individual substances in the thermodynamic system, only those that minimize the thermodynamic potential of the system, correspond to equilibrium values.
- (2) Of all the permissible values of the energy added by each independent component (atom), those maximizing the total contribution of energy of individual atoms to the system, correspond to equilibrium values.

The components of the system are all possible and existing substances in different aggregate states, which are formed from the elements included in the system under study. The substances which are minimum necessary for forming of this system are called thermodynamic system components. The number of components equals the number of substances in the system minus the number of independent reactions bonding these substances. At TM compounds with a multiple number of atoms forming them are considered to be condensed individual substances.

* Corresponding author. Tel.: +7 343 3608065; fax: +7 343 3751510.

E-mail address: 3608113@mail.ru (N. Barbin).

Substances with fractional stoichiometric coefficients are assumed to be solutions. Condensed phases include compounds in the solid (crystalline or amorphous) and liquid states. Individual compounds, which have the same chemical formula, but enter into different phases, are assumed to be different composite substances. The components of the gas phase are molecules, radicals, atoms, ions, and electron gas.

Extensive thermodynamic parameters of the system, i.e. those proportional to the amount or mass of substance in the system, are volume V , entropy S , internal energy U , enthalpy H , free energy F ($F = U - TS$), and Gibbs energy G ($G = H - TS$). Intensive thermodynamic parameters, i.e. those independent of the quantity or mass of the system, are pressure P , thermodynamic temperature T , concentration, and mole and specific thermodynamic values.

Two independent parameters out of V, S, U, H, P, T, F and G and the complete original chemical composition of the system should be assigned for explicit representation of any thermodynamic system. Each pair of the independent parameters defines a characteristic function, which is “the function describing the state of the thermodynamic system of the corresponding thermodynamic parameters, whereas this system is characterized by the fact that all its thermodynamic properties can be expressed explicitly by this function and its derivatives with respect to the thermodynamic parameters” [9].

The criterion of attainment of the equilibrium state by the system is the extremum of its characteristic function. If the parameters P and T are independent, the characteristic function is the Gibbs free energy G , while the minimum of this energy in the system (G_{min}) is the criterion for reaching of the equilibrium state. Taking the parameters U and V , the characteristic function in the isolated system is the entropy S , while the maximum entropy of the system, S_{max} , is the criterion for reaching of the equilibrium state.

One of the most efficient computation programs is the TERRA program package, which is the development of the ASTRA 4 soft [6].

The calculation algorithm in this program package was developed on the basis of the following assumptions of the mathematical model:

- The point in question is closed and isolated thermodynamic systems which boundaries are impermeable to the exchange of matter, heat and work with the environment.
- Systems in the state of the external and internal thermodynamic equilibrium (complete or local) are analyzed.
- The system under study is heterogeneous and consists of several homogeneous parts (phases) separated by visible interfaces.
- The gas phase should be necessarily present in the system.
- All the gaseous individual substances (atoms, molecules, atomic and molecular ions, electron gas) are parts of one gas phase.
- The gas phase is described by the ideal gas law.
- The surface effects at the interface are disregarded; gases do not dissolve in condensed (liquid and solid) phases; there can be no condensed substances.
- Condensed substances form single-component immiscible phases or are parts of ideal condensed solutions.
- The individual substances, which have the same chemical formula, but enter into different phases, are assumed to be different components.
- The substances, which have the same chemical formula, but are in different polymorphous modifications, the crystalline or liquid state, are regarded as one component which properties change abruptly at transformation temperatures.
- The volume of condensed components is negligible.

In accordance with the second law of thermodynamics, the equilibrium of such systems is characterized by the maximum entropy (S_{max}) relative to thermodynamic degrees of freedom, which include the concentration of components in an equilibrium mixture (M_q , mol/kg), the temperature T and the pressure P :

$$S = \sum_{i=1}^K \left[S_i^0(T) - R \ln \frac{RT}{V} n_i \right] \cdot n_i + \sum_{c=1}^{\tilde{N}} S_c^0(T) n_c + \sum_{n=1}^N \sum_{m=1}^{N_m} \left[S_m^0(T) - R \ln(n_m/n_{nm}) \right] \cdot n_m \Rightarrow S_{max} \quad (1)$$

where n_i , n_c , n_m , S_i^0 , S_c^0 and S_m^0 denote the number of moles and the standard entropy (at a temperature T and pressure of 10^5 Pa) in the gas (i) and condensed (c) phases, and in the solution (m), respectively; K is the quantity of gaseous components in the thermodynamic system; C is the quantity of condensed components in the thermodynamic system; N is the quantity of solutions in the thermodynamic system; n_{nm} is the quantity of substance moles in the m -th condensed solution; N_m is the amount of substance in the m -th condensed solution; V is the specific volume; R is the universal gas constant.

The specific volume V and the internal energy U remain to be independent variables since the conditions of the system equilibrium relative to the environment can be expressed as the equalities:

$$dV = 0 \text{ and } dU = 0 \text{ or } V = \text{const and } U = \text{const.}$$

The following additional restrictions are imposed on the tolerance range of variables when the chemical and phase equilibria are established through achievement of the maximum entropy.

- (1) The total internal energy (U) of the system is constant at equilibrium:

$$U - \sum_{i=1}^K U_i n_i - \sum_{c=1}^{\tilde{N}} U_c n_c - \sum_{n=1}^N \sum_{m=1}^{N_m} U_{nm} n_{nm} = 0 \quad (2)$$

where U_i , U_c and U_{nm} denote the total internal energy of gaseous, condensed components, and solution per mole:

$$U = \int_{T_0}^T C_{V\varepsilon} dT + \Delta_f H^0(T_0) \quad (3)$$

here $\varepsilon = i, c$, and m . $\Delta_f H^0(T_0)$ is the formation enthalpy at T_0 ; C_V is the heat capacity determined at a constant volume.

- (2) Conservation of the mass of all the chemical elements:

$$-M_j + \sum_{i=1}^K v_{ji} n_i + \sum_{c=1}^C v_{jc} n_c + \sum_{n=1}^N \sum_{m=1}^{N_m} v_{jnm} n_{nm} = 0 \quad (4)$$

where M_j is the mole content of the j -th chemical element in the system; v_{ji} , v_{jc} , and v_{jnm} are the numbers of atoms of the j -th element in the gaseous and condensed components of the system and the solution, respectively.

- (3) Charge conservation law:

$$\sum_{i=1}^K q_{ei} n_i = 0 \quad (5)$$

where q_{ei} is the degree of ionization of the i -th component (for the electron gas $q_{ei} = -1$).

- (4) The equation of state of a mixture of ideal gases:

$$pV - RT \sum_{i=1}^K n_i = 0 \quad (6)$$

where p is the pressure.

The parameters of the thermodynamic system equilibrium are determined by solving a mathematical problem of finding the extremum, taking into account all the restrictions and using the Lagrangian function [1]. The calculations are made by the Newton's method of successive approximations, which provides a high rate of convergence of results at the final stages of the iterative process.

The TERRA program package offers the following opportunities:

- Assignment of conditions of the equilibrium between the thermodynamic system and the environment by any pair of the six thermodynamic parameters: P (pressure), V (specific volume), T (temperature), S (entropy), H (enthalpy), and U (internal energy).
- Calculation of the equilibrium state of the thermodynamic system of an arbitrary elemental composition.
- Any individual substances can be included as anticipated components of the equilibrium composition by altering only input data.
- Determination of the equilibrium phase composition of the system without specifying in advance thermodynamically permissible states.

Thus, to determine the specific parameters of the system state, it is necessary to assign its two characteristics (e.g. P and T , V and T , H and P , etc.), the weight contents of the chemical elements in the working medium, and a list of individual substances potentially possible in equilibrium, specifying their thermodynamic functions – the entropy and the enthalpy.

The TERRA program package can also take into account some imperfections: to exclude any individual substances from the list of equilibrium components; to assign (fix) the concentration of one or several substances with the subsequent calculation of the equilibrium by the remaining part of the system; to consider non-ideal condensed solutions by assignment of the excess Gibbs energy; to take into account the volume occupied by condensed materials.

The phase composition and the equilibrium characteristics are calculated using the IVTANTERMO database on properties of individual substances. The database is a component of the program package. The contents of the database are mostly thermodynamic, thermophysical and thermochemical properties of individual substances systematized at the Institute of High Temperatures of RAS [10], the US National Bureau of Standards, published in the handbook [11], and calculated at Moscow State Technical University, using molecular, calorimetric and spectroscopic data. The database is open for users and allows spread-out and updating of the information.

Pb–Bi melts are represented by the model of ideal solutions of interaction products (model ISIP [12]). Condensed Bi, Pb, PbBi, Pb₃Bi₄, Pb₃Bi₅, Pb₃Bi₇, and PbBi₇ are included into this composition. The formation of these compounds was confirmed by Lyakishev [13]. The intermetallic compounds in the lead–bismuth melt are described by thermodynamic properties and functions of compounds Pb_xBi_y at the melt temperature. The mixing heats (ΔH_{mix}) between [Pb], [Bi] and groups [Pb_xBi_y] are accepted to be equal to zero, and the entropies of mixing (ΔS_{mix}) are calculated as for ideal solutions.

At TM the concentration of the intermetallic compounds in the melt is defined by the equilibrium state of the system, i.e. the pre-set parameters (for example, P and T) and the original ratio of Pb, Bi and Ar. Besides, TM also reveals equilibrium concentrations of all the gaseous components of the system, resulting from a of complex chemical and phase transformations.

The equilibrium concentrations of the condensed and gaseous components represent products of all the possible reactions between [Pb], [Bi] and [Pb_xBi_y] and the gas phase at reaching of

the global extremum of the thermodynamic potential by the system (S_{max}) [12].

The vapors of Pb, Bi, Pb₂, Bi₂, Bi₃, Bi₄, electron gas (e-gas) and ionized vapors of lead and bismuth are considered to be parts of the investigated gas phase.

The results of the thermodynamic modeling for Pb and Bi are similar to experimental data on the vapor pressures for pure lead and bismuth [14–17].

The liquid–vapor phase diagram for the Pb–Bi system at different pressures, obtained by TM using the model of the ideal solution of interaction products for the metal melt, is close to Volodin's experimental data [5]. In the article [5] phase boundaries of the lead–bismuth metal solution have been defined on the vapors pressure by the jet method. It is the evidence of adequacy of our approach to TM.

3. Results and discussion

The vapor pressures of the Pb–Bi melts were studied under an argon atmosphere and in the temperature and concentration intervals for the liquid state on phase diagrams.

The equilibrium state of the Pb + Bi + Ar system at general pressures of 10, 10², 10³, 10⁴, 10⁵, 10⁶, 10⁷ Pa and of nine various original compositions of the Pb–Bi alloy within 10–90 wt.% were simulated in the temperature range of 500–3000 K. The content of argon in all the systems was constant and it was equal to 40 wt.%.

The gas–vapor phase compositions were defined for each studied system.

The temperature dependences of the equilibrium partial pressures of the components of the gas phase at the fixed composition of the 40Ar + 30Pb + 30Bi (wt.%) system are shown in Figs. 1–6.

The basic component of the gas phase over the range of temperatures of 500–3000 K is argon. The argon pressure is constant and does not depend on temperature and the melt composition (according to the modeling conditions). Other components of the gas phase are vapors of Pb and Bi, dimers of Pb₂ and Bi₂, and also Bi₃, Bi₄, electron gas and ionized vapors of lead.

The major components after argon are lead and bismuth vapors. Their partial pressures exceed 10^{−1} Pa at temperature of 920 K and 10² Pa at 1280 K. The greatest content of these components in the gas phase (more than 10⁴ Pa) is attained after the temperature of the full melt evaporation (about 1800–1900 K). The significant

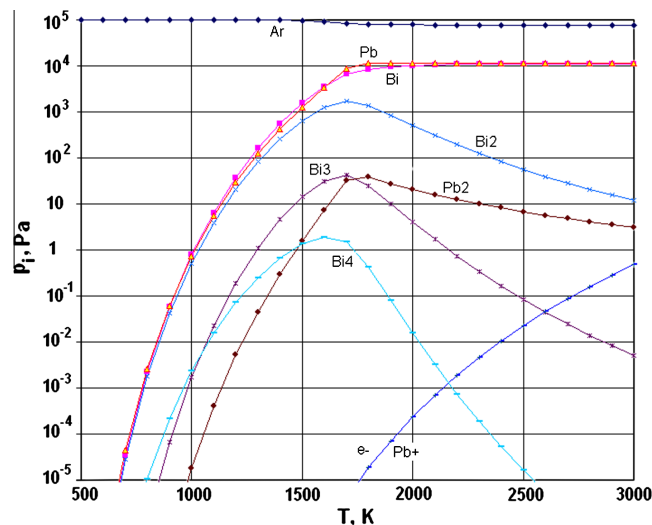


Fig. 1. Temperature dependences of the partial pressures of the components of the gas phase in the 40Ar + 30Pb + 30Bi (wt.%) system at 10⁵ Pa.

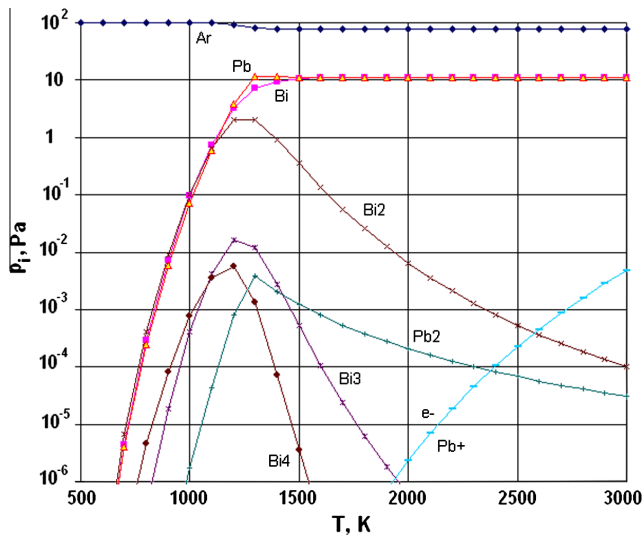


Fig. 2. Equilibrium composition of the gas phase in the 40Ar + 30Pb + 30Bi (wt.%) system at 10^2 Pa.

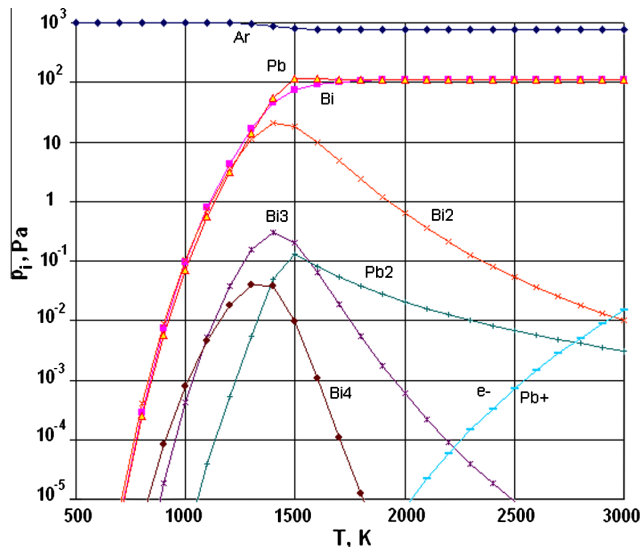


Fig. 3. Equilibrium composition of the gas phase in the 40Ar + 30Pb + 30Bi (wt.%) system at 10^3 Pa.

change of the content of Pb and Bi vapors in the gas phase does not occur any more at temperatures above 1900 K, what is presumably connected with increase of the role of reactions of the metal vapor ionization with the formation of electron gas and metal ions (Fig. 1).

The partial pressure (p_i) of the Pb vapors reaches 10^4 Pa at a temperature of 1740 K and a pressure of 10^5 Pa. The partial pressure (p_i) of the Bi vapors is 10^4 Pa at a temperature of 1950 K. The maximums of the partial pressures of Bi_2 and Bi_3 are observed at a temperature of about 1700 K. The maximums of the partial pressures of Bi_4 and Pb_2 are fixed at temperatures of ~1600 and 1750 K, respectively (Fig. 1).

The increase of the bismuth content in the Pb–Bi system leads to the growth of the partial pressures of the Bi, Bi_2 , Bi_3 , Bi_4 vapors and to the decrease of the partial pressures of the Pb, Pb_2 , Pb^+ vapors at a pressure of 10^5 Pa.

The partial pressures (p_i) of the Pb and Bi vapors reach 10^4 Pa at temperatures of 1300 and 1450 K, respectively, and at a pressure of

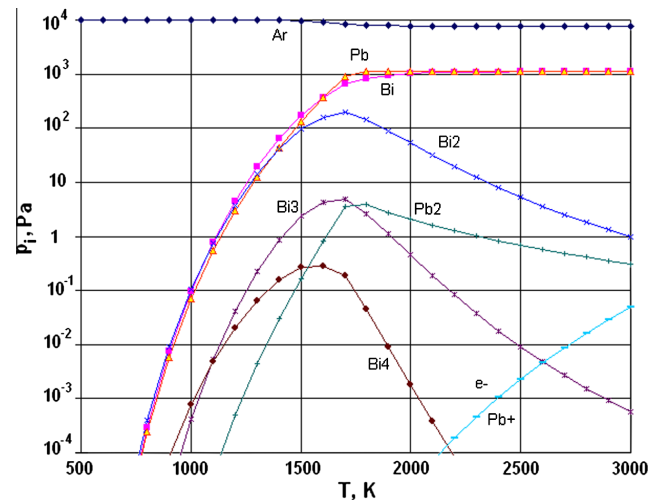


Fig. 4. Equilibrium composition of the gas phase in the 40Ar + 30Pb + 30Bi (wt.%) system at 10^4 Pa.

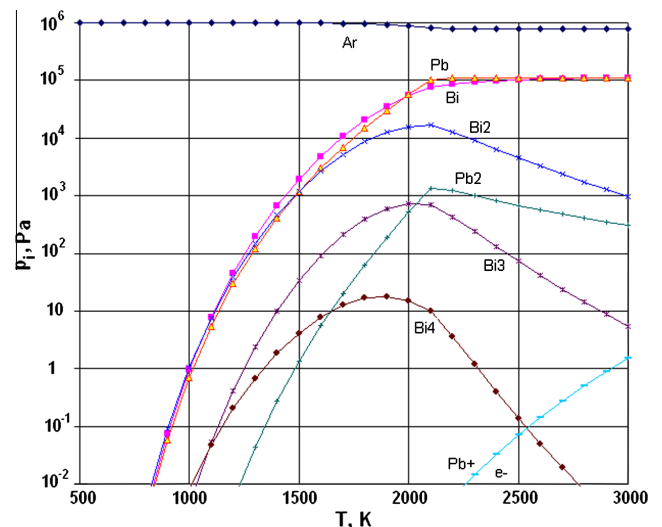


Fig. 5. Equilibrium composition of the gas phase in the 40Ar + 30Pb + 30Bi (wt.%) system at 10^6 Pa.

10^2 Pa. The greatest partial pressure (p_i) of Bi_2 is observed at a temperature of about 1250 K. The maximums of the partial pressures of Bi_4 and Pb_2 are fixed at temperatures of ~1200 and 1350 K, respectively (Fig. 2).

The partial pressures (p_i) of the Pb and Bi vapors reach 10^4 Pa at temperatures of 1450 and 1650 K, respectively, and at a pressure of 10^2 Pa. The greatest partial pressures of Bi_2 and Bi_3 are observed at a temperature of ~1400 K. The maximums of the partial pressures (p_i) of Bi_4 and Pb_2 are fixed at temperatures of ~1300 and 1500 K, respectively (Fig. 3).

The partial pressures of the Pb and Bi vapors reach 10^3 Pa at temperatures of 1750 and 1950 K, respectively, and at a pressure of 10^4 Pa, and the maximums of the partial pressures of Bi_2 and Bi_3 are attained at ~1700 K. The greatest partial pressures of Bi_4 and Pb_2 are fixed at temperatures of ~1600 and 1800 K, respectively (Fig. 4).

The partial pressures of the Pb and Bi vapors reach 10^5 Pa at temperatures of 2100 and 2400 K, respectively, and at a pressure

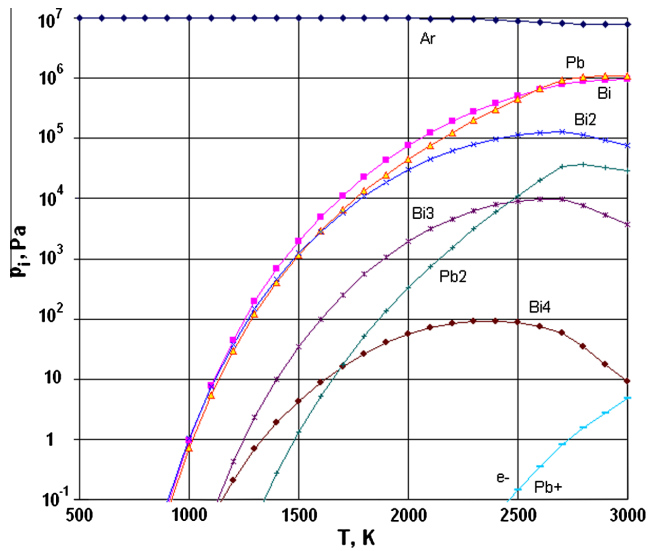


Fig. 6. Equilibrium composition of the gas phase in the 40Ar + 30Pb + 30Bi (wt.%) system at 10^7 Pa.

of 10^6 Pa. The maximums of the Bi_2 , Bi_3 , Bi_4 and Pb_2 partial pressures are attained at about 2100, 2050, 1900, and 2100 K, respectively (Fig. 5).

The partial pressures of the Pb and Bi vapors reach 10 Pa at temperatures of 2750 and 3000 K, respectively, and at a pressure of 10^7 Pa. The maximums of the Bi_2 , Bi_3 , Bi_4 and Pb_2 partial pressures are attained at about 2700, 2650, 2350 and 2350 K, respectively (Fig. 6).

The figures show that the equilibrium pressure increase in the system leads to the following changes:

- (1) Higher equilibrium pressure in the system leads to a significant increase of the full evaporation temperature of the melt (the shift reaches from several hundreds to thousands of Kelvin degrees).
- (2) The general pressure increase leads to the wider temperature interval of the melt evaporation; the equilibrium partial pressures of the gas components of the system increase more slowly with temperature rise at high pressures than at low pressures.
- (3) Higher equilibrium pressure leads to a considerable shift of the temperature interval of achievement of the maximum equilibrium partial pressures of the Pb_2 , Bi_2 , Bi_3 , Bi_4 vapors; the form of curves with the maximum becomes very wide, the ascending and descending parts of the curves are considerably stretched on the temperature axis.
- (4) At high pressures the values of the equilibrium pressures of Pb_2 and Bi_3 greatly increase, and the equilibrium partial pressures of Bi_2 and Bi_4 decrease. The pressure rise leads to the increase of the evaporation temperature of the melt.

The simulated phase diagrams of the liquid–vapor transitions for the Pb–Bi system under the Ar atmosphere and at various pressures are given in Fig. 7.

The reduction of the value of the equilibrium pressure leads to the narrowing of the liquid–vapor coexistence region on the temperature axis. It is proved by the experimental data of the research [5].

The highest extent of agreement of the carried out calculations with the data of the work [5] is observed in case of the use of the ISIP model for the systems with low equilibrium pressure. A small divergence of results of our calculations with the experimental data [5] (for the case when $P = 10^5$ Pa) is probably explained by

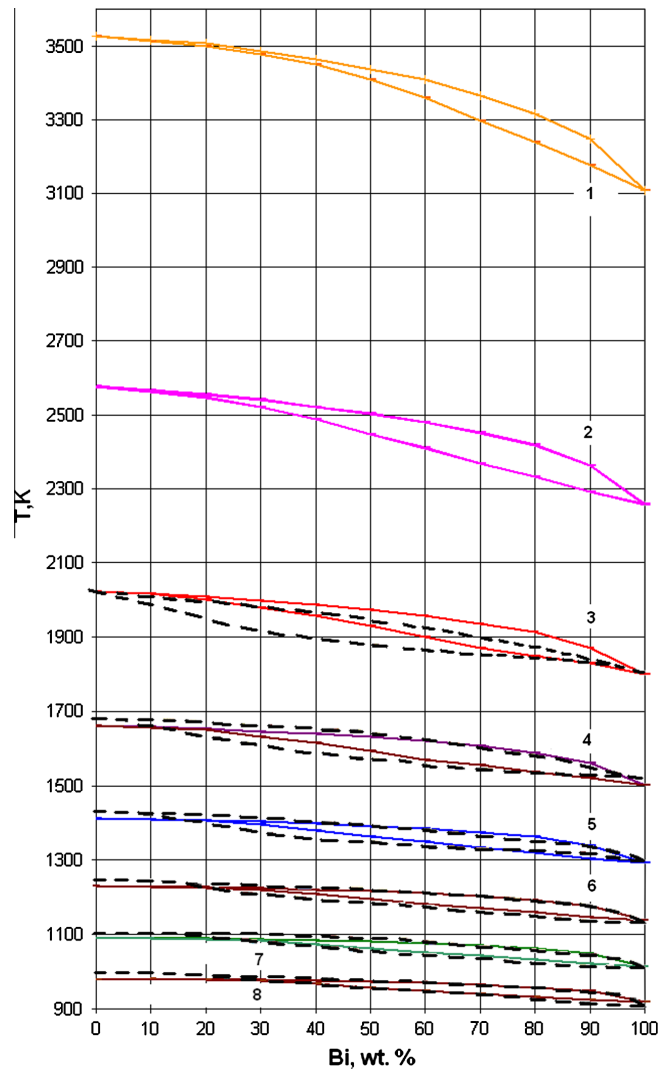


Fig. 7. Phase diagrams of the Pb–Bi system (liquid–gas interface) at various pressures (1– 10^7 Pa, 2– 10^6 Pa, 3– 10^5 Pa, 4– 10^4 Pa, 5– 10^3 Pa, 6– 10^2 Pa, 7–10 Pa, 8–1 Pa). The dashed lines are the experimental data [5], the solid lines – the thermodynamic modeling for the ISIP model.

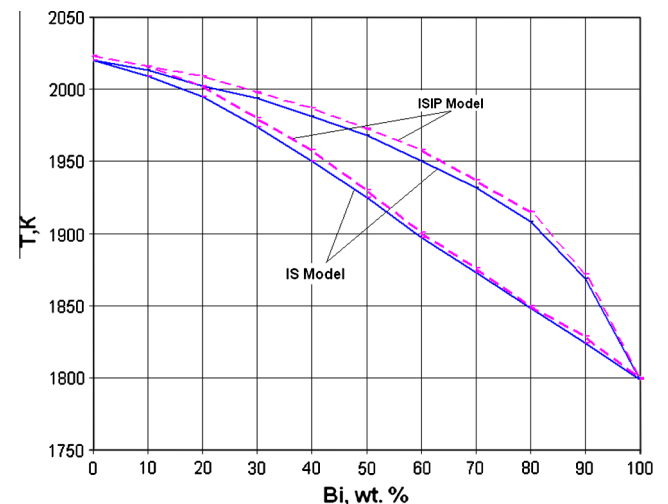


Fig. 8. Effect of the melt model on the form of curves of the phase diagram for the Pb–Bi system (liquid–gas interface) at 10^5 Pa.

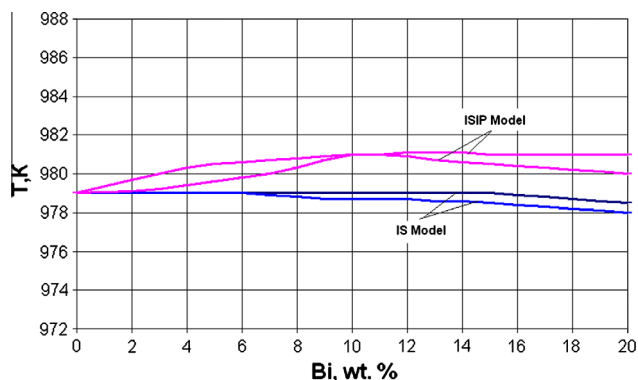


Fig. 9. Fragment of the Pb–Bi phase diagram (liquid–gas interface) for the IS and ISIP models at 1 Pa.

accumulation of errors of measurements in the high-temperature experiment. May be for this reason the experimental temperature of the full evaporation of pure bismuth at atmospheric pressure has appeared the lowest [5] in comparison with the data of other researchers [14–17].

The application of the ideal solution model (IS model) instead of the ISIP model at TM leads to the change of the form of curves of the melt–vapor phase transition (Fig. 8). The curves of liquid–vapor phase transitions become more convex by using of the ISIP model. It indicates that evaporation occurs at higher temperatures, than in case of using of the IS model (Fig. 8).

The thermodynamic modeling of the liquid–vapor phase transition for the Pb–Bi melt with application of the ISIP model at pressures of 1, 10, 100 Pa in the region of 1–20 wt.% Bi shows that there is a maximum (Fig. 9). There is no such maximum at modeling with the use of the IS model (Fig. 9).

4. Conclusion

The ISIP model is applied to the calculation of the composition of the gas phase, the evaporation temperatures, the partial pressures of the gas components for the Pb–Bi melt at various pressures. The diagrams of the liquid–vapor phase equilibria are constructed. The obtained results can be used for calculations of safety parameters of heat-transfer heavy metals for nuclear power units.

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